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Compositional Analysis by Spark Discharge in Argon Optical Emission Spectroscopy (SDAR-OES)

1 Introduction

The concentrations of selected elements in metallic objects can serve to chemically characterize their source. The concentrations of the elements intentionally added to an alloy are controlled by manufacturers to impart specific metallurgical properties required for a given product. Intentionally added elements are commonly specified to fall within a particular concentration range for a given alloy. Other elements are specified at maximum levels which the manufacturer may not exceed but which may otherwise vary considerably. Such variations in elemental concentrations provide a means for differentiating among the same alloy produced by different manufacturers and for distinguishing among specific production runs made by a single manufacturer.

Spark Discharge in Argon-Optical Emission Spectroscopy (SDAR-OES) is a destructive technique that can be used for quantitative compositional analysis of alloys. The SDAR-OES is used to produce validation data for alloy systems, establishing a limit of quantitation (LOQ) for various components within those systems. In an alloy system for which validation data has been generated, SDAR-OES can measure elements above the established LOQ, typically in the parts per million (ppm) range.

2 Scope

This document applies to case working personnel who perform metallurgical analyses. This procedure serves as a general guideline for all FBI Laboratory procedures that involve the use of SDAR-OES.

General procedures for quantitative compositional analysis by SDAR-OES are described below. Operational procedures for specific alloy classes or sample sizes are detailed in supplemental standard operating procedures (SOPs).

3 Principle

Application of this SOP to forensic materials requires knowledge of general concepts of optical emission spectroscopy (OES) analysis and specific instrument operation instructions. This knowledge can be obtained from the references provided, training from manufacturers or principal operators within the Lab, or schools covering theory and/or instrument operation.

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SDAR-OES has its basis in quantum mechanics. Electricity is used to heat a small surface region of the sample to a plasma state where elemental photons of characteristic wavelengths (energies) are ejected as visible or ultraviolet (UV) light. Photons are filtered to form a parallel beam which impacts a grating and is reflected at unique angles depending on the wavelengths present. Each photon strikes one of many detectors depending on its angle of reflection. The electronic reaction is converted to a digital signal which is processed to determine the energy of the striking photon. Many such emission and collection events are measured during a single experiment. Quantitative determination of individual elemental concentrations is achieved by comparing measured emission intensities to the manufacturer-determined calibration curves resident on the instrument's computer system.

The analysis is performed by machining a flat surface on the specimen, placing it on the plasma spark stand and completing an electrical circuit arc-spark protocol predetermined by the instrument software for the alloy class being analyzed.

4 Specimens

This procedure can be used for the analysis of metal alloy classes for which the instrument has been validated. Samples must be large enough to completely cover the analysis area to permit their examination by the method outlined here. The surface to be analyzed must also be flat with any nonmetallic debris removed.

5 Equipment/Materials/Reagents

a. SpectroLab LAV M10 spectrometer, or equivalent

b. Optic re-profiling standard

c. Standardization samples provided by the instrument manufacturer

d. Sample preparation equipment specific to the alloy class being analyzed (see 8.1 Prepare Samples)

e. High purity argon

f. One or more certified reference materials (CRMs) matrix-matched to the alloy class being tested

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g. Spark stand insert (waveguide), tungsten carbide electrode and wire brush dedicated to the alloy class being tested

h. Small sample spark stand plate with insert, 6 mm diameter opening (optional)

i. Vacuum cleaner with precision nozzle attachment

j. Lint-free wipes

6 Standards and Controls

Manufacturer-provided standards are used for re-profiling and standardization. The standardization samples to be employed in this procedure are specific to the alloy class being analyzed. Proper standardization is verified using one or more CRMs in the same alloy class. These CRMs are chosen by the operator to demonstrate adequate performance of the instrument on the elements of interest in a particular analysis.

7 Sampling

If large numbers of physically indistinguishable samples are received for compositional analysis, a sampling plan may be employed for testing. If the sampling plan will be used to make an inference about the population, then the plan will be based on a statistically valid approach. All of the samples may be tested at the examiner's discretion. Any sampling plan and corresponding procedure used will be recorded in case notes.

8 Procedure

8.1 Prepare Samples

Specimens measured by SDAR-OES must be flat and debris-free over the entire region of analysis. The method of specimen preparation for any specific alloy class is included in the method validation. Typically, steels are ground on zirconium oxide abrasive paper, cast irons are abraded using a swing grinder with Al_2O_3 abrasive, and softer, non-ferrous materials are turned on a lathe. Other methods of preparation may be suitable, but quantitative analysis must be validated for each preparation method. Optic re-profiling standards follow the steel preparation technique. Standardization samples follow the preparation method for the appropriate alloy class.

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8.2 Clean Instrument

a. Turn off power ("Source") to the spark stand. (Turn back on when cleaning/instrument check is complete.)

b. Assure that there is sufficient water in the system and that the air filter is not saturated with soot. Fill or exchange as necessary.

c. Inspect the spark stand components for soot accumulation. Vacuum if necessary.

d. If the spark stand components are changed in order to run a different alloy class, the spark stand must be thoroughly cleaned.

e. Prior to running the re-profiling program, run a 'dummy' sample of the same alloy class (steel) to flush out any residual oxygen and nitrogen in the system. This is especially important if the instrument has just been cleaned. More than one dummy analysis may be run to ensure that the elemental readings are stable.

8.3 Re-profile Optic

a. Verify that the proper spark stand components for the re-profiling standard (electrode and spark stand insert) are installed in the spark source stand.

b. Follow the manufacturer's instructions to run the re-profile procedure to optimize alignment of the optics. A minimum of five measurements is recommended.

c. Print the re-profiling results and retain them in the log accompanying the instrument.

8.4 Standardize

a. Run the standardization procedure within the appropriate method for the alloy class chosen based on the evidence to be analyzed. A minimum of five readings per standard is recommended.

b. Print the standardization results and retain them in the associated case file. Record the results of the standardization in the instrument log.

8.5 Analyze

a. Verify standardization with CRM(s) using the appropriate, standardized method

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for the selected alloy class. Follow surface preparation in 8.1 Prepare Specimens, if needed. A minimum of five readings per standard is recommended.

b.   If the CRM results do not agree with the certification, the instrument may be re-standardized, or re-profiled then re-standardized, to optimize performance.

c.   Print the CRM results and retain them in the associated case file.

d.   Prepare an appropriately sized area on the evidentiary item(s) (see 8.1 Prepare Specimens).

e.   Follow the instrument's instructions for sample analysis. Take at least five measurements on each sample. Save and print the concentration data from individual measurements as well as the average and standard deviation of the collected measurements.

f.   Rerun one or more of the CRMs, taking a minimum of five measurements per CRM, to create pre- and post-test comparison(s) to determine if any instrument drift has occurred.

g.   Print the post-test CRM results and retain them in the associated case file.

9 Instrumental Conditions

The instrumental conditions are set by the instrument manufacturer and are not normally changed or modified by FBI Laboratory personnel.

10 Decision Criteria

In general, it is expected that the mean concentration values determined by the instrument on a given CRM will be within the range of values indicated on the certificate of analysis. If a measured element fails to give adequate agreement with the CRM, the instrument can either be re-standardized to improve the agreement or, if the value is not critical, it may be regarded as a semi-quantitative value. The following process is used for the comparison of data from samples thought to share a common origin. *If only the alloy composition is required, this section can be omitted.*

The average weight concentrations (wgt %) of a given element in two samples are inter-compared using a pooled t-test statistic of the type detailed in 11 Calculations. The

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concentrations are deemed to be "analytically indistinguishable" if the concentrations in the two samples differ by less than the preselected critical t value. This procedure is repeated for each of the elements present in the sample. Critical t values are chosen so that an $\alpha = 0.05$ can be achieved for the overall analysis. Only elements above the LOQ are considered in calculating "α". $\alpha = 1 - [P(\ |t| \leq t_{critical}\ )]^r$ where "r" is the number of elements present above the quantitation limit, P is the probability of observing a t-value of less than or equal to $t_{critical}$ and α represents the approximate cumulative probability of calling two samples analytically distinguishable when they are not.

For example, suppose 15 elements are above the LOQ, then choosing ($t_{0.9966} = t_{critical}$) yields an $\alpha = 0.05$. This means there is a 5.0% chance of incorrectly rejecting a match between any two samples when one actually exists. Note that repetitive means testing requires a relatively high critical value of t. In contrast, for a $t_{0.99}$, $\alpha = 0.14$ leading to a relatively high rate of false rejection (14%).

Segregation, surface depletion and microstructural banding may also need to be considered in evaluating alloy sources. Constituents that do not completely solutionize are especially prone to inhomogeneous distribution. Consequently, these may potentially exhibit unusually high t-test values. Because these effects depend on the prior processing history, generalizations often cannot be applied. The examiner may make a determination that two samples are associated to a given degree based on inspection of the analytic data and considerations of the possible sources of compositional variation in the material.

11 Calculations

11.1 Quantitative Analysis

The measured emission intensity of each element of interest is compared to the emission intensity of a selected matrix line and the system calibration curves. This data is used to determine the weight percentage of each of the elements present. Quantitation of the data is performed automatically by the system program and is not directly controlled by the user.

11.2 Comparative Analysis

Where quantitative data from two specimens are being compared, a pooled, two-tailed, Student's t-test statistic of the sample means is typically used for the comparison. Two samples are deemed to be "indistinguishable" in the property under consideration if the two samples differ by less than the preselected critical t value ($t_{critical}$). The critical t values are typically chosen so that an overall, (Bonferroni-corrected) value of $\alpha = 0.05$ can be achieved for the analysis and are determined by the degrees of freedom associated with the measurement. An $\alpha = 0.05$ means

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there is a 5.0% chance of incorrectly rejecting a match between two samples when one actually exists.

To perform this test, the means and variances of each sample are determined as follows:

The mean value: $\bar{x}_a = \dfrac{\sum\limits_{i=1}^{n_a} x_i}{n_a}$ where $\bar{x}_a$ is the average value of the measurements on sample "a",

$\sum x_i$ is the sum of the individual measurements and n_a is the number of measurements made on that sample. The variance of the individual measurement values from sample "a" is given by:

$$s_a^2 = \frac{\sum\limits_{i=1}^{n_a}(x_i - \bar{x})^2}{n_a - 1}$$

The mean and variance of the data from sample "b" are calculated in the analogous manner.

The pooled sample variance is then calculated as: $s_p^2 = \dfrac{(n_a - 1)s_a^2 + (n_b - 1)s_b^2}{(n_a + n_b - 2)}$

A standard two-tailed statistical test of the two sample means is performed.

If $\left| \dfrac{(\bar{x}_a - \bar{x}_b)}{\left(\sqrt{s_p^2(\frac{1}{n_a} + \frac{1}{n_b})}\right)} \right| > t_{critical}$ for any point of comparison, the samples are concluded to have a

statistically significant difference. If not, the samples are concluded to be indistinguishable.

Typically five or more measurements per sample are used for performing comparisons.

12 Measurement Uncertainty

Quantitative data from this procedure are generally used for comparative purposes. Expanded uncertainty should not be used for these inter-comparisons because it increases the probability two samples will appear to be analytically indistinguishable and therefore increases the likelihood of type II errors (false inclusion).

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When quantitative data are compared to a particular specification or when quantitative elemental compositions are reported and it is necessary to determine the expanded uncertainty of a measurement, it will be calculated in accord with the *Chemistry Unit Procedures for Estimating Measurement Uncertainty*. Measurement uncertainty associated with a particular element can vary depending on alloy class, concentration of the element of interest, and the concentrations of other elements present in the alloy, so uncertainties must be calculated on a case-by-case basis.

13 Limitations

The estimated limits of quantitation (LOQ) have been determined for each alloy class validated and are listed in the specific alloy class SOPs. In general, these values have been found to correlate well with those observed in practice using CRMs (where these are available). However, some day-to-day variation is expected and values approaching the LOQ are best regarded as semi-quantitative unless standards are available to confirm the LOQs in a particular instrumental run. Data below the LOQ are to be used only in a qualitative fashion due to the inherent uncertainty associated with them. For example, the absence of manganese from a steel sample would be an important qualitative result due to the ubiquitous presence of this element in steels.

For elements in the range 0.1-100 wgt %, the relative standard deviation (rsd) will typically be less than 5%. For elements in the range of 0.01-0.1 wgt %, the rsd is typically than less than 15%. Below 0.01 wgt % but above the LOQ, rsd's of up to 30% are to be expected though less than 10% is typical. Insoluble elements will frequently give higher than expected standard deviations due to their inherently inhomogeneous distribution in a given sample.

If higher relative standard deviations than those cited above are experienced, attempts can be made to correct the problem by re-machining the surface of the sample and retesting.

14 Safety

a.   Review pertinent material Safety Data Sheets (SDS) prior to machining and testing samples. Analyze the composition of an unknown metal sample by non-destructive means (e.g., x-ray fluorescence analysis) prior to SDAR-OES analysis. If additional guidance is required, contact the Laboratory Health and Safety Group.

b.   Wear safety glasses when machining samples and cleaning and operating the SDAR-OES instrument to prevent eye injury. Additionally, wear lab coat and gloves when cleaning the instrument and changing the air filter.

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15 References

Thomsen, V. B. E, *Modern Spectrochemical Analysis of Metals - An Introduction for Users of Arc/Spark Instrumentation*, ASM International 1996

Slickers, K., *Automatic Atomic-Emission-Spectroscopy, 2nd Ed.*, Bruhlsche Universitatsdruckerei, Germany 1993

Milton, J. S. and Arnold, J. C., *Introduction to Probability and Statistics - Principles and Applications for Engineering and Computer Sciences, Fourth Edition*, McGraw-Hill Higher Education 2003

Chemistry Unit Quality Assurance and Operations Manual, Federal Bureau of Investigation, Laboratory Division, latest revision

FBI Laboratory Operations Manual, Federal Bureau of Investigation, Laboratory Division, latest revision

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Rev. #	Issue Date	History
0	03/02/2018	Original issue. Relevant general information was taken from 401-7 *Analysis of Carbon and Low Alloy Steel Samples by Spark Discharge in Argon Optical Emission Spectroscopy*, 402-4 *Analysis of Small Carbon and Low Alloy Steel Samples by Spark Discharge in Argon Optical Emission Spectroscopy*, and 403-4 *Analysis of Copper by Spark Discharge in Argon Optical Emission Spectrometry*.

Approval   Redacted - Signatures on File

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QA Approval

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